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AUTHOR(S):

Ikada, Eiji

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REVIEW

## Dielectric Properties of the Oligomers of Chain Polymers

Eiji IKADA\*

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Dielectric properties of the low-molecular-weight chain polymers (the so-called "Oligomer") in pure liquid state are investigated to elucidate the relaxational phenomena of segmental motion of a long chain molecule in rubbery state. Almost all of the dielectric relaxations of long chain molecules show asymmetric arcs on Cole-Cole plane. The empirical Havriliak-Negami equation

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau_0)^{1-\alpha}]^\beta}$$

is applied to these relaxations observed to obtain relaxational parameters and the applicability of the equation is discussed. The distribution parameter of relaxation times of the oligomers of poly(vinylacetate) of which degree of polymerization is ca. 5 is not smaller than that of high-polymeric poly(vinylacetate) as expected, on the other hand, width of distribution of relaxation times of ethylene diamine oligomers increases as the chain length increases. Thus, there are two different kinds of oligomers. The dielectric relaxation of polymers ( $\alpha$ -relaxation) is due to segmental motion in a long chain, on the other hand, that of a small polar molecule is attributed to rotation as a whole. The purpose of this study is to find out critical point in the transition of relaxational mode from molecular rotation as a whole to microbrownian motion of chain segment by varying chain length of polymers.

KEY WORDS: Dielectric relaxation/ Low-molecular-weight polymers/ Dependences of degree of polymerization/ Havriliak-Negami-type relaxation/ Cooperative relaxational mechanism/

### INTRODUCTION

A systematic discussion on properties of homologous organic compounds is very fascinating and available for a physico-chemist to understand properties of organic materials. For example, Fieser wrote in his book that boiling points of normal hydrocarbons increase linearly with the chain length. He also discussed on some other properties of organic homologues in terms of chain length<sup>1)</sup>.

Smyth collected the dielectric data of some organic homologues such as n-alkylbromide<sup>2)</sup>. According to his book, dependence of distribution constant  $\alpha$  for alkyl bromides upon the chain length does not change markedly until for 10 carbon atoms of the alkyl bromides. He analyzed this result by increasing twisting around the carbon-carbon bonds.

In this report, dielectric properties of some oligomers are studied to explain dielectric properties of polymers. In this study, low-molecular-weight poly(vinylacetate) and poly(methylmethacrylate) were synthesized by radical polymerization and several popular

\*篠 英之: Faculty of Engineering, Kobe University, Nada, Kobe 657 Japan

commercial oligomers such as propylene and ethylene glycol oligomers are mixtures of different chain length. These oligomers are high-viscous liquids at room temperatures.

It is necessary for such a large chain molecule to obtain large energy on molecular rotation as a whole. Then, the larger a chain is, it contains motional freedom the more. Molecular entanglement leads to the high viscosity of the oligomers. Spherical structure is impossible for such a long chain and a rod-like structure is probable. This rod-like structure also leads to higher viscosity than a spherical molecule does.

End group in an oligomer chain plays an important role in its properties. Such an end effect is almost negligible for a high polymeric system. For example, the low-molecular-weight polypropylene glycol having hydroxyl group in the both chain ends shows high viscosity, on the other hand, the same molecule having acetoxyl end groups shows much lower viscosity.

Dielectric investigators often make use of Cole-Cole plots for better understanding of relaxational properties of matters. By glancing at this experimental plot, we can easily know various kinds of relaxational parameters such as distribution of relaxation times. Up to this time, dielectric relaxations have been observed for a lot of materials, for example, solids, liquids. These observed relaxations are roughly classified into the four types of dielectric relaxations according to distribution of relaxation times. These are Debye-, Cole-Cole-, Davidson-Cole- and Havriliak-Negami-type relaxations as follows<sup>3)</sup>:

Debye-type

$$\epsilon^* - \epsilon_\infty = \epsilon' - j\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau_0} \quad (1)$$

Cole-Cole-type

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}} \quad (2)$$

Davidson-Cole-type

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{(1 + j\omega\tau_0)^\beta} \quad (3)$$

Havriliak-Negami-type<sup>4)</sup>

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau_0)^{1-\alpha}]^\beta} \quad (4)$$

where  $\epsilon^*$  is complex dielectric constant,  $\epsilon_0$  and  $\epsilon_\infty$  are the limiting low- and high-frequency dielectric constants, respectively, and  $j$  is the imaginary unit, and  $\omega$  is angular frequency, and  $\tau_0$  is average relaxation time;  $1-\alpha$  and  $\beta$  are the distribution parameters of relaxation times.

On the other hand, Williams et al. suggested an empirical equation which expresses well experimental asymmetric dielectric relaxations of polymers<sup>5)</sup>.

Williams-Watts-type relaxation:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left[ -\frac{d\phi(t)}{dt} \right] \exp(-i\omega t) dt$$

where  $\phi(t)$  is the empirical decay function:

$$\phi(t) = \exp - (t/\tau_0)^\beta; \quad 0 < \beta \leq 1.$$

The dielectric relaxations of the polyhydroxyl alcohol such as 2,4-pentanediol show the Davidson-Cole-type relaxation represented by eq 3. This type of relaxation is observed for many diols and triols<sup>6,7)</sup> liquids, however, their relaxational mechanism is not yet definitely clarified. Results of the dielectric relaxations showing asymmetric arcs are numerous and symmetric relaxations often seen in monoalcohols, on the other hand, are rather exceptional. It is considered that relaxational mechanisms associated with asymmetric relaxation is regarded as being associated not with simple motion like molecular rotation but with cooperative mechanism combined with the two simultaneous motions. It seems, therefore, that reasonable cooperative mechanism must be discussed.

### EXPERIMENTAL

#### Synthesis of oligomers

Definition of "Oligomer" is somewhat ambiguous and arbitrary. Only the "Oligomers" which are viscous liquid at room temperatures are studied. Their degree of polymerization is smaller than 30.

The methods of synthesis are radical polymerization and the details are described in each report. The literature numbers, end groups, and degree of polymerization are summarized in Table 1. Several highly viscous oligomers are commercially obtainable. Ethylene and propylene glycol oligomers (for example, PPG Diol 400 etc.), ethylene diamine oligomers and ethanolamine oligomers are commercial products. Purification of oligomers are generally difficult, but some of them could be distilled into each pure portion.

Table 1. Degree of polymerization and end groups of oligomers

oligomer	degree of polymerization*	end groups	literature
MMA-I	3.01	(CH <sub>3</sub> ) <sub>2</sub> CO-, -H	ref 14
MMA-II	3.01	Cl <sub>2</sub> -, -Cl	ref 13
VAC-I	4.7	CH <sub>3</sub> CO-, -H	ref 14
VAC-II	3.0	Cl <sub>2</sub> C-, -Cl	ref 13
1,2,6-hexanetriacetate			ref 8
glyceryltriacetate			ref 8
2,4,6-heptanetrioltriacetate	trimer model molecule of PVAc		ref 14
(syndiotactic, isotactic, heterotactic)			
NBR-1		HOOC-, -COOH	ref 9
acrylonitrile			
NBR-2		HS-, -SH	"
butadiene			
copolymer			
NBR-3	47 (ML <sub>1+4</sub> , 100°C)		"
NBR-4	75 (ML <sub>1+4</sub> , 100°C)		"
poly(ethyleneglycol)	1, 2, ..., 6	HO-, -OH and CH <sub>3</sub> COO-, -OOCH <sub>3</sub>	ref 20
poly(propyleneglycol)	"	"	ref 20, ref 21

\* Molecular weight of the oligomers was determined by vapor pressure osmometry

### Dielectric measurement

Dielectric constants and losses are measured by means of a transformer ratio-arm bridge (type TR-1BK, Ando Electric Co.). The frequency range covers from 10 Hz to 3 MHz. The dielectric cell is a platinum concentric glass cell of which vacuum capacitance is 13.0 pF. The cell is calibrated in advance by using the standard dielectric liquids. The cell was immersed in a water bath at higher temperatures and in an alcohol bath at lower temperatures and accuracy of temperature control is within  $\pm 0.5^\circ\text{C}$ .

### Method of determination of relaxation parameters of the Havriliak-Negami equation

The limiting low-frequency dielectric constant  $\epsilon_0$  and the limiting high-frequency dielectric constant  $\epsilon_\infty$  are obtained by extrapolating the experimental locus to the low- and high-frequency intercepts on the real axis, respectively.

The real and imaginary parts of eq 4 are given by

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) r^{-\beta/2} \cos \beta\theta \quad (4a)$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) r^{-\beta/2} \sin \beta\theta \quad (4b)$$

with

$$r = [1 + (\omega\tau_0)^{1-\alpha} \sin \alpha(\pi/2)]^2 + [(\omega\tau_0)^{1-\alpha} \cos \alpha(\pi/2)]^2 \quad (4c)$$

and

$$\theta = \tan^{-1} \left[ \frac{1 + (\omega\tau_0)^{1-\alpha} \cos \alpha(\pi/2)}{(\omega\tau_0)^{1-\alpha} \sin \alpha(\pi/2)} \right] \quad (4d)$$

Dividing eq 4b by eq 4a, the following relationship is obtained

$$\tan \phi = \frac{\epsilon''}{\epsilon' - \epsilon_\infty} = \tan \beta\theta \quad (5)$$

Using eq 4d, we can deduce the following relationship

$$\lim_{\omega\tau_0 \rightarrow \infty} \tan \theta = \lim_{\omega\tau_0 \rightarrow \infty} \tan(\phi/\beta) = \tan(\phi_L/\beta) = \cot \alpha(\pi/2) \quad (6)$$

Hence

$$\phi_L = (1 - \alpha)\beta(\pi/2) \quad (7)$$

where  $\phi_L$  is the high-frequency limiting angle made by the experimental locus with the real axis.

The relaxation time  $\tau_0$  is obtained by determining the crossing point of the bisector of the asymptotic angle  $\phi_L$  with the locus. This crossing point corresponds to the relaxation frequency  $(1/2 \pi\tau_0)$ . The distribution parameter  $(1 - \alpha)$  is obtained from the following relationship

$$\frac{1}{\phi_L} \log \frac{|\epsilon_{(\omega\tau_0=1)}^* - \epsilon_\infty|}{\epsilon_0 - \epsilon_\infty} = -\frac{1}{\pi(1 - \alpha)} \log [2 \sin \alpha(\pi/2)] \quad (8)$$

where  $|\epsilon_{(\omega\tau_0=1)}^* - \epsilon_\infty|$  is the distance between  $\epsilon_\infty$  and  $\epsilon_{(\omega\tau_0=1)}^*$ .

Table 2. Distribution parameters(1- $\alpha$ ) and  $\beta$  and relaxation time  $\tau_0$ .

oligomer	temp./°C	1- $\alpha$	$\beta$	$\tau_0$
NBR-1	-40.0	0.690	0.520	$1.23 \times 10^{-2}$
	20.8	0.856	0.555	$7.96 \times 10^{-8}$
NBR-2	-30.5	0.799	0.459	$4.19 \times 10^{-6}$
	-1.6	0.773	0.624	$2.04 \times 10^{-6}$
NBR-3	-10.0	0.494	0.634	$3.70 \times 10^{-4}$
	16.0	0.689	0.544	$9.65 \times 10^{-7}$
NBR-4	2.0	0.604	0.464	$5.30 \times 10^{-2}$
	18.0	0.609	0.565	$4.75 \times 10^{-5}$
poly(vinylacetate)*	70.0	0.902	0.556	...
glyceryl triacetate	-58.1	0.915	0.523	$2.65 \times 10^{-3}$
	-39.1	0.982	0.484	$1.33 \times 10^{-6}$
1,2,6-hexane triacetate	-60.5	0.945	0.525	$5.69 \times 10^{-4}$
	-30.7	0.936	0.487	$3.12 \times 10^{-7}$
isotactic PMMA**	90.1	0.645	0.385	...
	63.0	0.530	0.320	...
MMA-I	20.1	0.586	0.451	...
	0.1	0.590	0.437	...

\* Relaxation parameters were calculated from the numerical values of Ishida et al.<sup>11)</sup>.

\*\* The data of PMMA are cited from ref 16.

Distribution of relaxation times and relaxation times of the oligomers studied are collected in Table 2.

## RESULTS AND DISCUSSION

### Applicability of Havriliak-Negami equation

Experimental arcs on complex Cole-Cole plot for all of the oligomers studied were tried to compare with the calculated arcs of the Havriliak-Negami equation. Good coincidence is seen as is shown in Figures 1 and 2. All the other experimental results of the dielectric relaxations are also well expressed by this equation which is, therefore, considered to be appropriate equation for the dielectric relaxation already observed because this Havriliak-Negami-type relaxation contains the Debye ( $\beta=1-\alpha=1$  in the Havriliak-Negami equation), the Cole-Cole ( $\beta=1$ ), the Davidson-Cole ( $1-\alpha=1$ ) equation.

The real and imaginary parts of complex dielectric constants are given from eq 3 by

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) (\cos \phi)^\beta \cos \beta\phi$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) (\cos \phi)^\beta \sin \beta\phi$$

where  $\tan \phi = \omega\tau_0$ . Putting  $\theta = \tan^{-1} [\epsilon''/(\epsilon' - \epsilon_\infty)]$ , then  $\tan \theta = \tan \beta\phi$ , or  $\omega\tau_0 = \tan(\theta/\beta)$ .

For the Davidson-Cole-type dispersion, plots of  $\log \tan(\theta/\beta)$  against  $\log$  frequency should give a straight line with the slope of unity. This plot was tried for glyceryl triacetate and 1,2,6-hexane triacetate<sup>9)</sup>. Fig. 3 shows this result. It is clear that  $\log$  frequency vs.  $\log \tan(\theta/\beta) =$

$$\log \tan [\beta^{-1} \tan^{-1} \epsilon''/(\epsilon' - \epsilon_\infty)] \text{ for the two acetates}$$

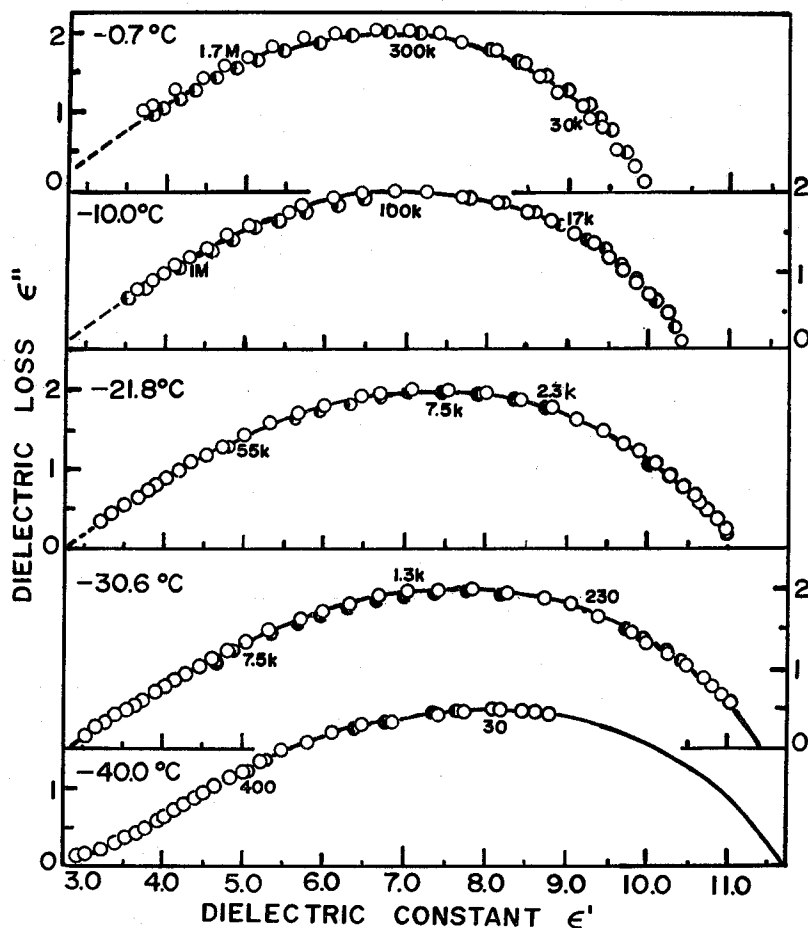


Fig. 1. Cole-Cole plots for NBR-1: (○) observed points; (◐) calculated points; numbers refer to frequency in Hz.

cannot be represented by linear relationship. Then the Havriliak-Negami equation was applied. Fig. 1 and Fig. 2 show the dielectric relaxations of NBR-1 and NBR-3. Hollow circles are experimental and half black circles are points calculated by the Havriliak-Negami equation<sup>9)</sup>. The agreement between the experimental and the calculated points is fairly good.

#### Dielectric properties of poly(vinylacetate) and its related compounds

Dielectric properties of poly(vinylacetate) (PVAc) were first reported by Fuoss<sup>10)</sup>. He showed that the shapes of the  $\alpha$ -relaxation of PVAc well resemble the calculated curves of the Davidson-Cole-type relaxation. Ishida et al.<sup>11)</sup> also precisely tested applicability of the Davidson-Cole empirical equation to the  $\alpha$ -relaxation of PVAc and reported that only small deviation is observed, but the arcs cannot be expressed by the Davidson-Cole equation.

It is, therefore, interesting to study molecular weight dependence of dielectric pro-

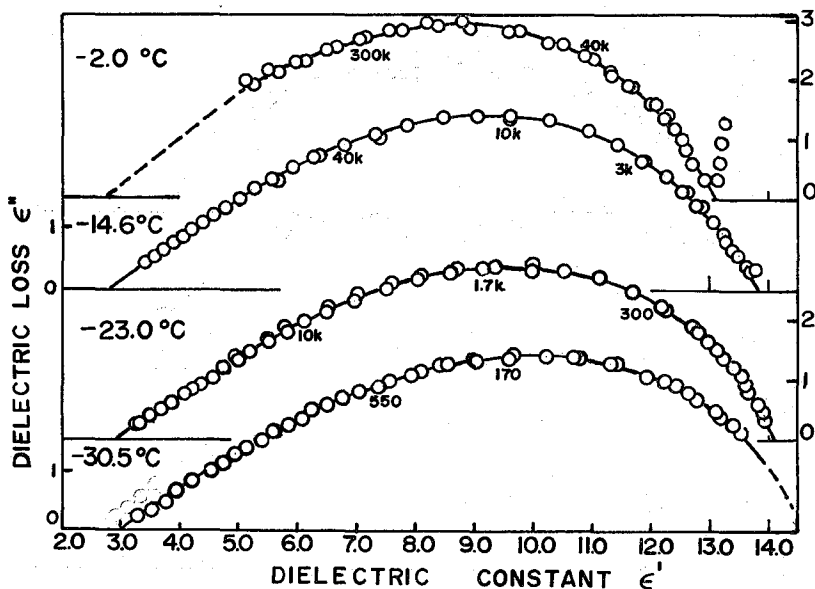


Fig. 2. Cole-Cole plots for NBR-3.

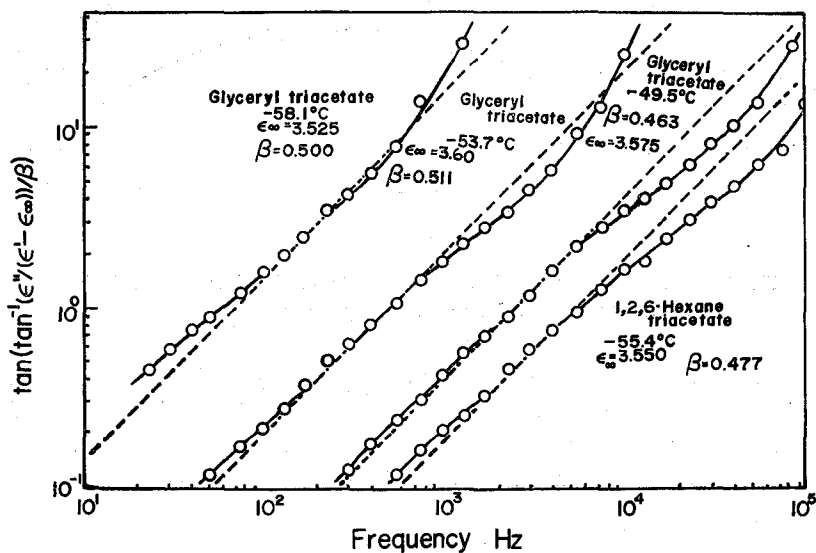


Fig. 3. Log  $\tan [\beta^{-1} \tan^{-1} \epsilon'' / (\epsilon' - \epsilon_{\infty})]$  vs. log frequency.

properties of various vinylacetate oligomers in order to know how the width of distribution of relaxation times of poly(vinylacetate) changes when its chain length decreases. Dielectric relaxations of the analogous molecules having more acetoxyl side groups than two, low-molecular-weight PVAc<sup>12,13</sup>, 2,4,6-hexanetriol triacetate<sup>14</sup>, 1,2,6-hexanetriol triacetate<sup>8</sup> and glyceryl triacetate<sup>8</sup> were studied. It was found from these studies that the acetates studied show the distribution of relaxation times characteristic of PVAc, VAc oligomers



and acetates. The value of distribution parameter  $\beta$  of the Havriliak-Negami equation for the acetate molecules studied is about 0.5 and  $1-\alpha$  is near 0.95 with the exceptions of VAc-I and VAc-II<sup>12,13</sup>. The molecular structure of the acetates may be related with the characteristic distribution of relaxation times. Figures 4, 5, 6, and 7 show the Cole-Cole plots of VAc oligomers and the acetate molecules.

As for molecular structure, the another important point deduced from all acetate molecules studied is that all of these acetates have acetoxy side groups more than two in a molecule. The bonding position of acetoxy group in skeletal carbon is not associated with the distribution.

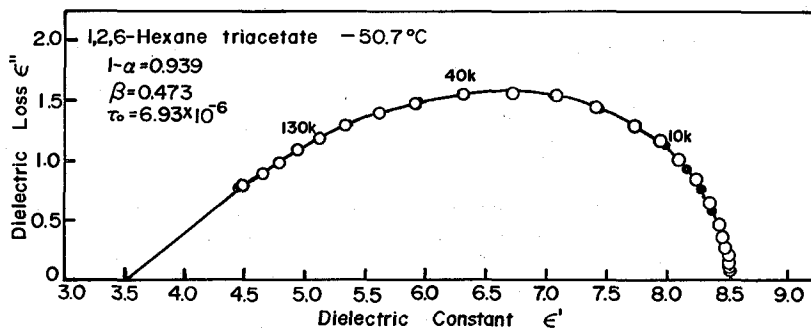


Fig. 4. Typical Cole-Cole plot for 1,2,6-hexanetriacetate: ○, experimental points; ●, calculated points.

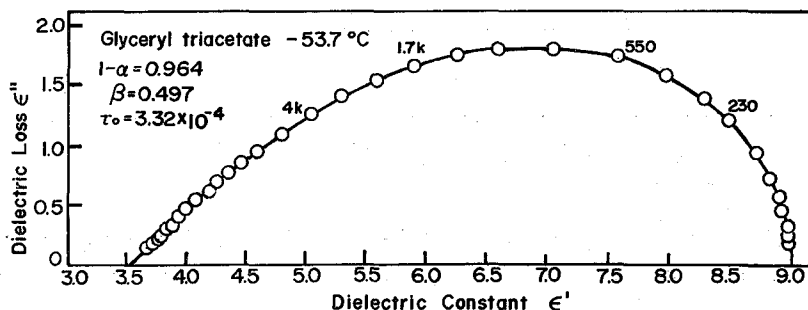


Fig. 5. Typical Cole-Cole plot for glyceryltriacetate. In this figure agreement between the calculated points and the experimental points is so good as to render them indistinguishable. The calculated points were therefore omitted from this figure.

#### Dielectric properties of MMA oligomers

It is well known that the segmental motion of main chain ( $\alpha$ -relaxation) and the side chain ( $\beta$ -relaxation) for poly(methylmethacrylate) (PMMA) are submerged in one absorption<sup>15</sup>. For this reason, the distribution of relaxation times is wider than that for  $\alpha$ -relaxation of a normal polymer such as PVAc because of superposition of the two different types of relaxations.

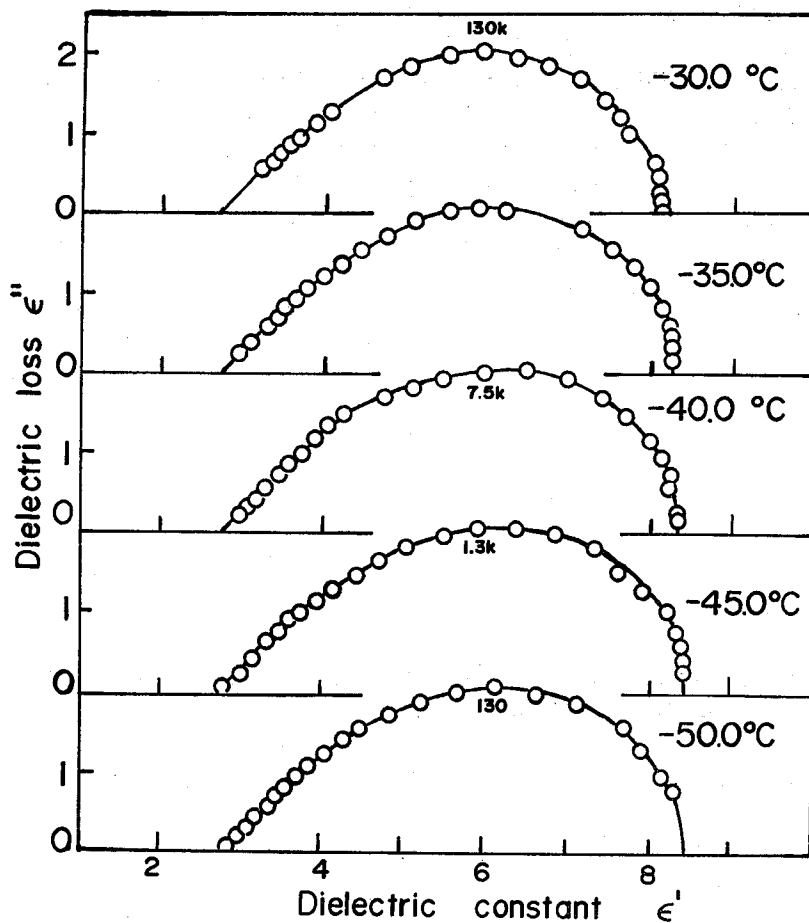


Fig. 6. Cole-Cole plots of isotactic 2,4,6-heptanetriol triacetate at various temperatures. Numbers appearing with data points denote frequencies in Hz.

Two different MMA oligomers having different end groups<sup>12,13)</sup> are synthesized as is shown in Table I. Fig. 8 shows the experimental complex arcs of the low-molecular-weight PMMA (MMA-I and MMA-II). Their degree of polymerization is 3.0 both for MMA-I and MMA-II. It is clearly seen from these arcs that the width of distribution of relaxation times is as wide as that of high polymeric PMMA<sup>16)</sup> although the degree of polymerization is much smaller than that for PMMA. This result leads to the conclusion that distribution of relaxation times does not depend on the chain length of a polymer but on the molecular structure of MMA monomer like the case of PVAc and the related molecules.

#### Dielectric properties of ethylene diamine oligomers $H_2N(C_2H_4NH)_nH$ ( $n=1, 2, 3$ and $4$ )

Relaxation behaviors of ethylene diamine oligomers<sup>17)</sup> are curiously different from those of VAc and MMA oligomers above described. As is shown in Fig. 9, the experimental Cole-Cole plots of the dimer (diethylene triamine  $H_2NC_2H_4NHC_2H_4NH_2$ ) and the

# Dielectric Properties of Oligomers

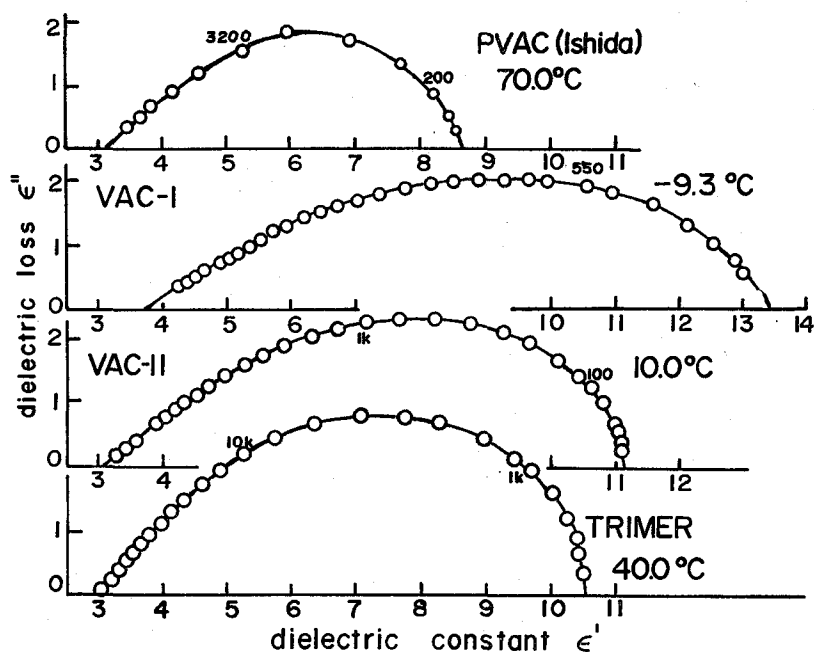


Fig. 7. Comparison of the Cole-Cole arcs for four different vinyl acetates.

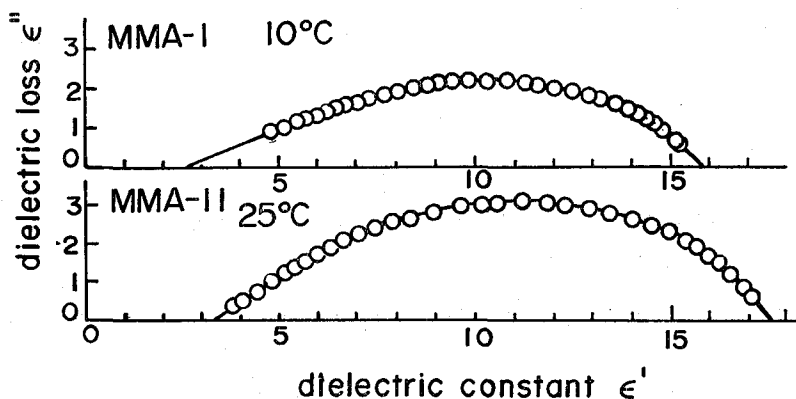


Fig. 8. Comparison of the Cole-Cole arcs of MMA-I and MMA-II.

tetramer (tetraethylene pentamine  $\text{H}_2\text{N}(\text{C}_2\text{H}_4\text{NH})_4\text{H}$ ) in pure liquid state do not fit the calculated curve of the Havriliak-Negami equation. Further, the distribution of relaxation times varies markedly with increase of degree of polymerization. The Cole-Cole arcs of aminoethylethanolamine  $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{OH}$  cannot be expressed by the Davidson-Cole equation<sup>18)</sup>. Thus, we can find abnormal dielectric properties in the amino chains. Inversion of nitrogen atom (umbrella-like motion) probably makes the relaxational behaviors of amino chains complicated.

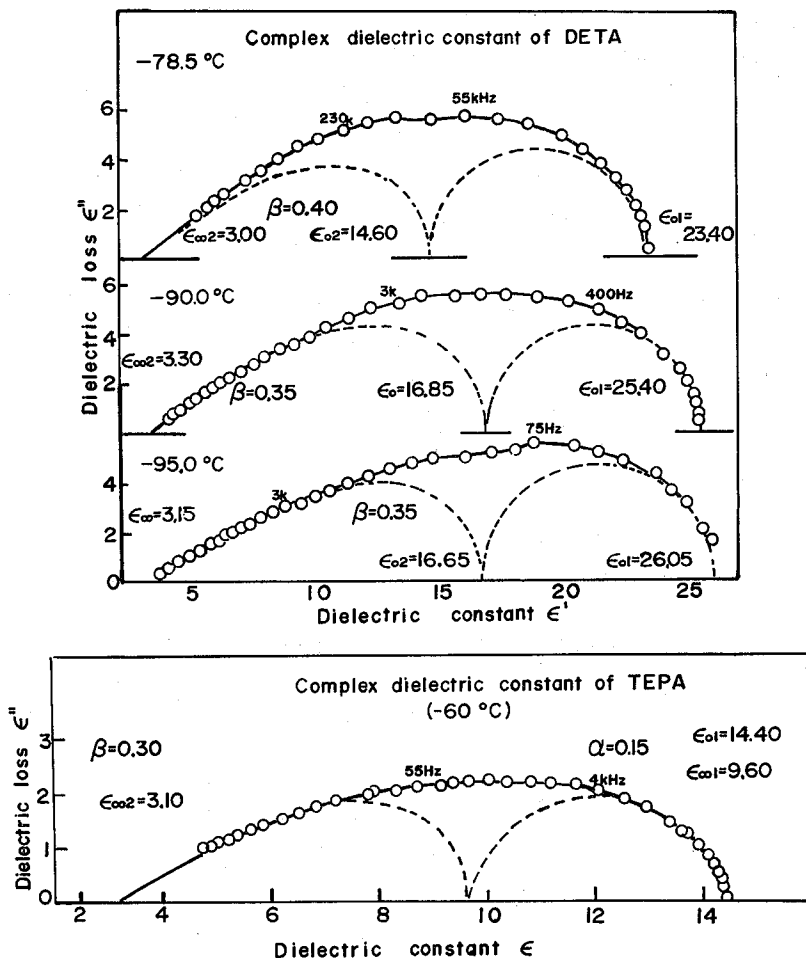


Fig. 9. Cole-Cole plots of diethylenetriamine (DETA) and tetraethylenepentamine (TEPA).

#### Effects of chain end group in the dielectric properties of an oligomer

Some of the oligomers studied have hydrogen bonding groups such as  $-\text{COOH}$  and  $-\text{OH}$  in their chain ends. The viscosity of propylene glycol oligomers having  $-\text{OH}$  group in both chain ends is much lower than that of the propylene glycol oligomers having  $-\text{COOCH}_3$  end groups as is seen Fig. 10<sup>19)</sup>. Difference of the viscosities between hydrogen bonding and non-hydrogen bonding propylene glycol oligomers (degree of polymerization = 34) is also seen<sup>20)</sup>. This chain is very long, therefore, possibility of intermolecular hydrogen bonding  $\text{OH} \cdots \text{O}$  is regarded as being very small, but this molecule has ether oxygen in the repeating unit  $(-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-)$  and the hydroxyl group in its both ends.

Fig. 8 shows the relaxation arcs of MMA-I (end groups =  $\text{CH}_3\text{CO}-$ ,  $-\text{H}$ ) and MMA-II (end groups =  $\text{CCl}_3-$ ,  $-\text{Cl}$ ) and Fig. 7 shows the arcs of VAc oligomers VAC-I (end groups =  $\text{CH}_3\text{CO}-$ ,  $-\text{H}$ , degree of polymerization = 4.7). VAC-II (end groups =  $\text{Cl}_3-$ ,  $-\text{Cl}$ ,

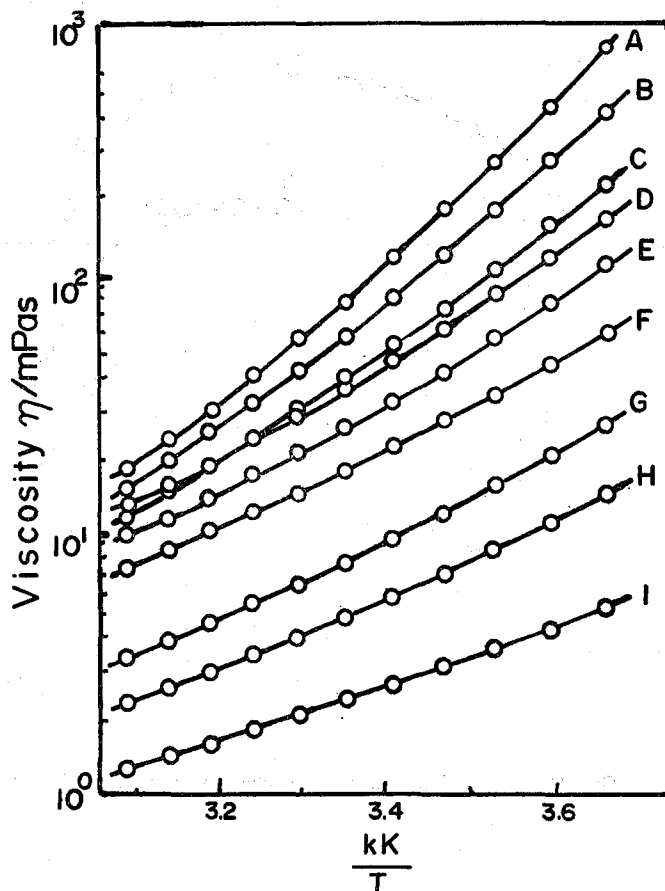


Fig. 10. Viscosities against the reciprocal of temperatures for ethylene, propylene glycol and propylene glycol diacetate oligomers: A, dipropylene glycol; B, tripropylene glycol; C, monopropylene glycol; D, triethylene glycol; E, diethylene glycol; F, monoethylene glycol; G, tripropylene glycol diacetate; H, dipropylene glycol diacetate; I, monopropylene glycol diacetate.

degree of polymerization=3.0). The shapes on Cole-Cole planes are clearly different depending on the structure of the end groups. It is difficult to explain this difference of distribution of relaxation times. The following two reasons are taken into account,

- 1) Due to existence of cooperative motions of the segmental motion of a main chain and the rotational motion of the polar end groups.
- 2) Defects of the chain near the chain ends on radical polymerization. The latter reason must be discussed further.

#### Dependences of chain length of diols on the distribution of relaxation times

Hydrogen bonding diols and triols show the Davidson-Cole-type relaxation<sup>6,7)</sup>, although monoalcohols show the Debye-type relaxation<sup>3)</sup>. Aminoethylethanolamine ( $\text{H}_2\text{NC}_2\text{H}_4\text{-}$

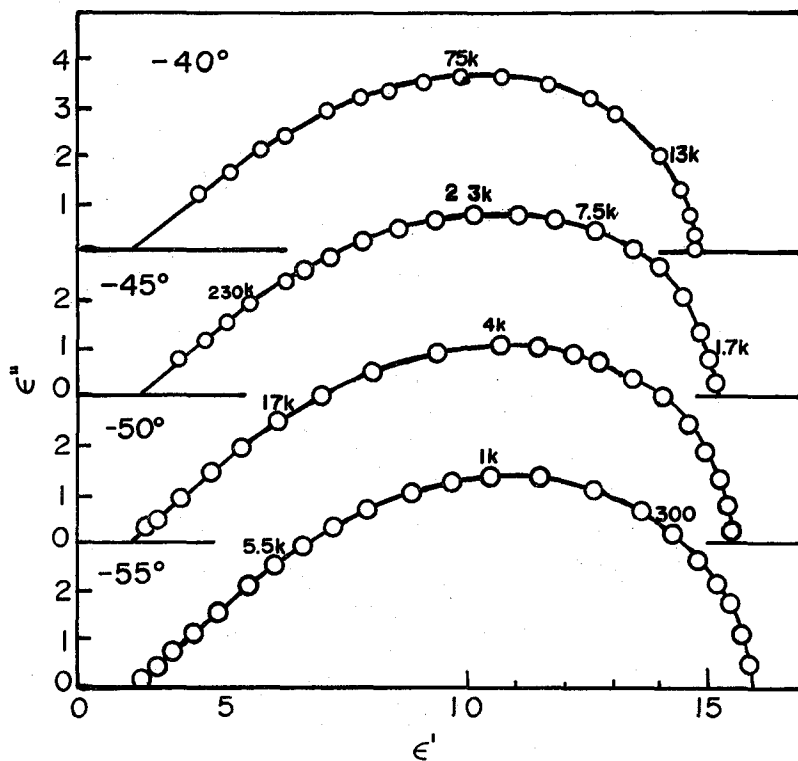


Fig. 11. Cole-Cole plots of pentapropylene glycol at various temperatures.

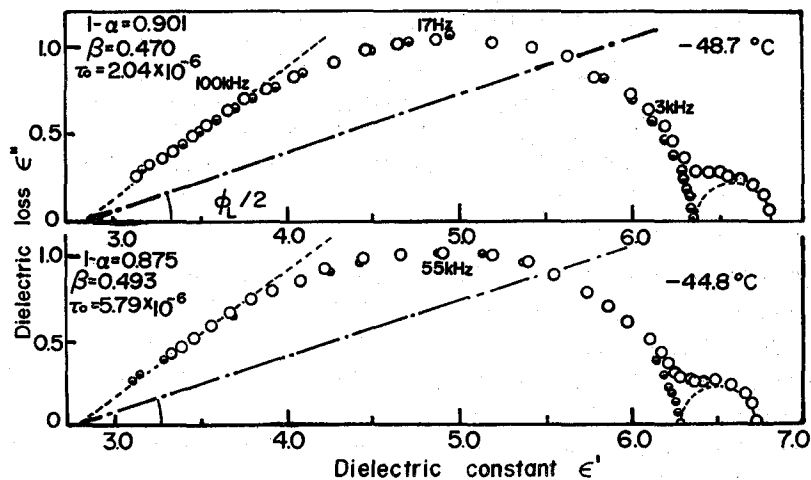


Fig. 12. Cole-Cole plots of complex dielectric constants of propylene glycol diacetate oligomer:  $\phi$  is the angle between the asymptote in the high-frequency region of the arc and the real axis.  $\circ$ , observed points;  $\bullet$ , calculated points; numbers beside data points refer to the measuring frequency in Hz.

$\text{NHC}_2\text{H}_4\text{OH}$ ) does not show the Davidson-Cole-type relaxation<sup>18)</sup>. Pentapropylene glycol<sup>20)</sup>  $(\text{HO}(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_5\text{H})$  is a comparatively long chain molecule and it shows the Davidson-Cole-type relaxation as is shown in Fig. 11. On the other hand, high-molecular-weight propylene glycol<sup>21)</sup> (average degree of polymerization=34) shows the Havriliak-Negami-type relaxation as is shown in Fig. 12. It seems that higher chain length limit in showing the Davidson-Cole-type relaxation is pentamer of propylene glycol.

Concerning of the dielectric properties of a small molecule, 2, 4, 6-heptanetriol triacetate and glyceryltriacetate, which are acetylated molecules of the corresponding diol and triol, do not show the Davidson-Cole-type relaxation as is shown in Fig. 4 and Fig. 5. This result leads to the conclusion that breaking and reforming of hydrogen bond plays an important role in the dielectric relaxation of diols and triols showing the Davidson-Cole-type relaxation. It is considered that the change from the Havriliak-Negami-type to the Davidson-Cole-type relaxation results from the similar behavior associated with the lack of distribution of relaxation times exhibited in the dielectric relaxations of monoalcohols.

#### Motional transition from molecular rotation as a whole to microbrownian motion of molecular segment

Under alternating electric field, a dipolar molecule must orientate to counteract surface charge of the two electrodes. Orientation of a polar molecule between the electrodes corresponds to rotation of a dipole.

Molecular reorientation as a whole becomes gradually impossible even in pure liquid state when molecular chain length becomes longer. For a high polymer, segmental motion of main chain is possible in rubbery state. Mobility of chain segment on microbrownian motion depends on free volume in rubbery matrix, but is hindered by C-C bond of a chain skeleton. It seems to be very difficult to find out clear transition from molecular rotation to limited segmental motion in relaxational phenomena by varying chain length continuously.

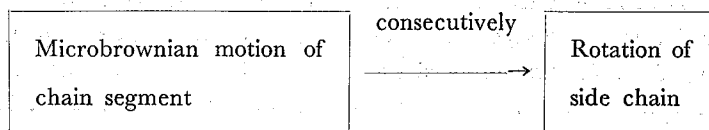
#### Asymmetry in distribution of relaxation times

Symmetric Debye-type arcs are observed in the dielectric relaxations of alkyl alcohols such as 1-propanol<sup>3)</sup> which shows no distribution of relaxation times even in pure liquid state. Diluted system of a polar small molecule in a non-polar solvent shows distribution of relaxation times. Dipolar motion accompanying breaking and reforming of  $\text{OH}\cdots\text{O}$  hydrogen bond via proton jump in a liquid monoalcohol is controlled by uniform potential barrier. On the other hand, it is difficult to explain the asymmetric distribution in bihydroxyl molecules such as 2, 4-pentanediol. Moreover, there is no marked difference between the dielectric properties of diols and triols. Therefore, Davidson-Cole-type relaxation cannot be attributed to existence of two hydroxyl groups. Almost all of  $\alpha$ -relaxations of chain molecules also show asymmetric distribution.

#### Hypothesis of "Consecutive Motion" in an oligomer

Asymmetric distribution is generally explained mathematically by consecutive mechanisms consisted of two motions. An oligomer as well as a polymer has several types of motional freedom, that is, rotation as a whole, twisting of molecular segment, rotation of

side group, etc. It is concluded from a lot of dielectric results that the molecules which show asymmetric relaxations contains more than two polar side groups in a molecule. The consecutive motion plays an important role in the dielectric relaxations of oligomers as follows.



Therefore, the superposed relaxation (for example, Relaxation A + Relaxation B) must be observed in the cooperative motion. In the consecutive motion of an oligomer, the segmental motion enhances consecutively the rotation of side chain, Glarum regards two mechanisms as dipolar orientation and diffusion of defects such as hole in liquid matrix<sup>22)</sup>.

### CONCLUSION

- 1) The polar oligomers studied are viscous liquids at room temperatures. They show dielectric relaxations due to microbrownian motion of molecular segment over the frequency range from 10 Hz to 3 MHz.
- 2) Molecular weight of the oligomers (degree of polymerization = 1 – 30) studied is much lower than that of a conventional high polymer ( $\bar{P} \geq 10^4$ ), but relaxation behaviors of the oligomers are not far from those of the corresponding high polymer. The experimental relaxation arcs on Cole-Cole plane are well represented by the empirical Havriliak-Negami equation. This equation is also applicable for the relaxations of small molecules.
- 3) Width of distribution of dielectric relaxation times does not decrease so largely as the molecular chain length decreases with the exceptions of ethylenediamine and ethanolamine oligomers. This fact shows that the width of distribution does not depend on chain length.
- 4) The distribution of relaxation times is associated with the molecular structure of the monomer unit of the oligomer.

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